

**The Development of an Improved Acoustic Apparatus for Determining
Vapour/Liquid Critical Points in Supercritical Fluids ¹.**

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ABSTRACT

This paper describes an apparatus designed to make precise semi-automated acoustic measurements on single, binary, and multi-component mixtures in the near and supercritical regimes, with excellent control of the temperature, pressure and homogeneity of the mixture. The automation greatly reduces the time required to carry out a set of measurements. The apparatus uses lead metaniobate piezoelectric transducers to make acoustic measurements in the frequency range of 0.5 MHz to 5 MHz, over a range of pressures (1-300 bar) and temperatures (0 °C to +100 °C). The temperature of the fluid is measured by platinum resistance thermometry. The apparatus has a variable volume and view ports to observe the critical behaviour of the mixtures. We have analysed the acoustic signals using cross-correlation techniques which provide greater precision in determining the sound velocity through the fluid, than using the unfiltered waveforms.

KEY WORDS: acoustic measurements; carbon dioxide; critical point; experimental method; sound velocity; supercritical fluids.

1. INTRODUCTION

The area of supercritical fluids (SCFs) has greatly expanded over the last few decades [1]. A supercritical fluid is a highly compressed fluid with the properties of both a liquid and a gas. Supercritical fluids have solvating powers similar to liquids thus making them extremely useful in extraction processes [2]. They also have gas-like abilities to travel through densely packed areas, enabling their use in chromatography. Recent advances in applications of supercritical technology have led to a whole new branch of chemistry and novel chemical reactions [3]. A chemical reaction involves at least three components (reactant, product and solvent). A major problem with supercritical chemistry is the difficulty encountered in following the behaviour of such multi-component fluids, as the reaction proceeds. Complete understanding of the reaction requires a full knowledge of the phase diagram of a range of compositions. Measurement of such a phase diagram requires considerable effort.

A simple acoustic method for measuring the critical point of a fluid has recently been reported [4]. Although this apparatus generates fairly accurate measurements, it relies on continuous human observation and recording of data to find the critical point.

The main aim of the present work is to develop semi-automated techniques for investigating the critical points of ranges of multi-component mixtures, critical points which can be difficult to predict accurately using theoretical methods and tedious or difficult to measure by visual inspection.

The acoustic apparatus, described here, provides digital control of temperature, pressure, and the acoustic measurements. Digital signal processing techniques allow the sound velocity to be determined accurately, as the pressure and temperature are accurately swept. The relative attenuation of the acoustic signal may be determined after applying

coupling corrections using the measured velocity and calculated density of the fluid.

2. BACKGROUND

For most single component fluids, for example pure CO₂, it is possible to detect the critical point visually by holding the density close to the critical density and then heating the fluid through the critical temperature. At the critical point, the density of the gas and the liquid become identical and the meniscus between the two phases disappears, a single phase forming. For carbon dioxide the critical point is at $P_c = 1071$ PSI (A) and $T_c = 31.1^\circ\text{C}$ [5-7]. Very close to the critical point, fluctuations in the density of the fluid occur which cause light to be scattered; viewed under white light the fluid appears to change from yellow to brown to black as the critical point is approached. However some heavier gases, which are used as refrigerants, do not have an easily detectable meniscus and visual inspection of the critical point is very difficult. When multi-component mixtures are used, the phase behaviour of the fluid can become far more complex [2], with the possibility of multiple critical points, not all of which will necessarily be readily observable using visual techniques. It is because of these complexities that the measurement of critical phenomena with acoustics is proving to be a useful tool, particularly when such measurements can be successfully automated.

During the very first experiments on critical phenomena Baron Cagniard de la Tour [8] observed strange acoustic effects when a fluid was heated through its critical point. Later investigations indicated that a minimum in the velocity and a maximum in the attenuation of sound occur at the critical point.

In a homogeneous ideal gas, the sound velocity is solely a function of temperature. In real gases however, the velocity also varies with the pressure. At sufficiently high

frequencies where heat conduction may be ignored, the sound velocity [9] is usually given by the formula,

$$w^2 = \left(\frac{\partial P}{\partial \rho} \right)_s = -V^2 \left(\frac{\partial P}{\partial V} \right)_s = -\mathcal{W}^2 \left(\frac{\partial P}{\partial v} \right)_T \quad (1)$$

Near the critical point, however, the gradient of the isotherm tends to zero, and γ tends to infinity. The product is indeterminate and an alternative expression must be considered.

The gradient of the isotherm may be expressed using,

$$\left(\frac{\partial P}{\partial V} \right)_s = \left(\frac{\partial P}{\partial V} \right)_T + \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial T}{\partial V} \right)_s \quad (2)$$

Using Maxwell's relations the expression for the sound velocity can then be written as,

$$w^2 = -V^2 \left(\frac{\partial P}{\partial V} \right)_T + \frac{TV^2}{C_v} \left(\frac{\partial P}{\partial T} \right)_V^2 \quad (3)$$

Here C_v is the specific heat at constant volume. At the critical point the isothermal compressibility tends to zero. Thus the first term in equation 3 vanishes leaving

$$w_{Crit}^2 = \frac{TV^2}{C_v} \left(\frac{\partial P}{\partial T} \right)_V^2 \quad (4)$$

It appears that the sound velocity should tend to zero, since C_v is predicted to have a weak divergence at the critical point. However, experimentally, the speed of sound is not

observed to reach zero at the critical point [10], but instead to exhibit a sharp minimum. This minimum is thought to be due to weak density gradients in the fluid due to gravity and, more fundamentally, to finite frequency scaling effects. Only in the limit of zero frequency would the velocity go to zero at the critical point, even in the absence of density gradients. In order to use the measurement of sound velocity to locate a critical point however it is essential that residual minima exist in the velocity measured along isotherms at temperatures above the critical point. Such minima exist in all the systems that have been examined so far.

The attenuation of a sound wave is predicted to pass through a maximum at the critical point [11, 12], due in part to scattering from the fluctuations in density which occur on all length scales. The attenuation close to the critical point may become so large that the signal is lost. However, the use of a sufficiently low frequency enables measurements to be made close to the critical point. The existence of residual maxima in the attenuation, in measurements along isotherms somewhat away from the critical temperature, also enables the critical temperature to be located from attenuation measurements.

3. STRATEGY FOR DESIGN AND MEASUREMENT

The objective of our semi-automated design is to provide a less labour intensive measurement of substantial regions of the phase diagrams of selected fluid mixtures and the accurate location of the critical points through the measurement of the acoustic velocity and attenuation. Human intervention is however required in specifying the regions to be investigated and in considering certain aspects of phase separation.

The apparatus must be capable of making measurements at precise pressures and temperatures, with very low temperature gradients. Any apparatus capable of holding

fluids at pressures of several hundred atmospheres must necessarily be massive, with a correspondingly high heat capacity. An appropriate measurement strategy in examining general regions of the phase diagram is therefore to make measurements along isotherms. Changing the pressure will in itself perturb the temperature very slightly and a suitable pace of measurement must be allowed for equilibrium to re-established. To determine the exact position of a critical point our strategy is first to stabilise the apparatus at a temperature just above the selected critical point and then to make measurements at appropriate pressure intervals along this isotherm. The computer software then identifies the pressure at which the velocity is a minimum. This pressure is then reset, and the corresponding volume maintained while further velocity measurements are made at constant density as the temperature is lowered extremely slowly. We expect the system to pass very close to the critical point in moving along this path on the phase diagram. The procedure may be repeated to refine the measurements; measurements are made along an isotherm corresponding very closely to the critical temperature, the volume is fixed at the value corresponding to the velocity minimum and the temperature slowly lowered again. It is more convenient to approach each critical point from above, although our apparatus is capable of detecting any phase separation, which presents a boundary within the ultrasonic cell.

To ensure the reliability of repeated operation we have opted to use two fixed ultrasonic transducers, rather than involve the very precise repeated translation of one of the transducers used by some previous workers [13]. Fixed transducers gives more than adequate precision in velocity measurement, but the observed attenuation is the sum of the attenuation in passing through the fluid and the coupling losses at the fluid - transducer interfaces. These coupling losses, which involve the acoustic impedance of the fluid ρw ,

change appreciably close to the critical point. However the attenuation in the fluid is very high close to the critical point and the relatively small changes in coupling can be estimated from the measured velocity and the known density of the fluid.

4. THE APPARATUS

A schematic diagram of the apparatus is shown in Fig. 1. The acoustic cell is contained inside a thermostatted copper enclosure from which the acoustic cell is very well thermally insulated. This enclosure is held at a stable temperature ($\pm 0.1\text{K}$) a few degrees below the temperatures of measurement. The insulation, combined with the use of heat shunts on major connections to the acoustic cell, ensures an extremely uniform temperature distribution. The temperature of the acoustic cell is itself stabilised to high precision. A computer controlled Wheatstone bridge is used, where one arm contains a number of thermistor temperature sensors connected in parallel. These sensors are distributed about the surface of the acoustic cell. An analogue three-term controller provides power to a number of distributed resistive heaters. This system is capable of a long term temperature stability of better than $\pm 2\text{mK}$. The temperature of the cell is measured independently using a calibrated platinum resistance thermometer, sensed by the computer through a digital ohm-meter.

The pressure of the cell is controlled by pumping a secondary fluid from the syringe pump (ISCO model 260D) into the top of the cell, where it acts against a piston which in turn acts on the fluid being measured. The fluid of the syringe pump is maintained at the temperature of the copper enclosure. The computer measures the pressure via a sensor attached to the cell close to the acoustic transducers.

The two acoustic transducers consist of identical discs of lead metaniobate [14], a

piezoelectric which is more heavily damped than the more commonly used PZT. We find that lead metaniobate gives cleaner pulse shapes than PZT when used with fluids of very different acoustic impedance to the transducer itself. The transmitting transducer is driven by a short sine-burst of 3-6 cycles at the fundamental frequency, or occasionally at an odd harmonic. Transducers with fundamental frequencies in the range 0.5-5 MHz are used. The received signal is amplified and fed to a digital oscilloscope and thus to the computer. The transducer assembly is demountable from the cell, and this allows transducer alignment and the determination of transducer spacing to be carried out in air before the assembly is mounted into the acoustic cell.

Two techniques are used to determine the pulse delay, and hence the velocity. The first method measures the delay between the start of the transmitted pulse (Fig. 2a) and the start of the received pulse (Fig. 2b), the absolute time of flight (Δt_{abs}). The envelope of the received pulse rises at the start of the received burst over a number of cycles however and the true start is often not available above the electronic noise, particularly close to a critical point when the attenuation is severe. The start of the received pulse is therefore determined by measuring the amplitudes of the first few observable cycles of the pulse and determining the start of the pulse from the ratios of a number of selected pairs. Preliminary tests show that the ratios of early peak amplitudes uniquely define the start of the pulse (Fig. 2c). These ratios are measured away from the critical point along with the time displacement of a zero crossing 2-3 cycles from the true start of the received trace. As the critical point is approached, the maxima and minima of the first few cycles (P_x and N_x) are monitored and the same zero crossing is identified and corrected by the same number of cycles as before to provide the start of the received pulse. This enables accurate measurement of the absolute time of flight. The validity of the method is tested further by

the measurement of a standard fluid for which the velocity is known. The second technique used is very powerful and is capable of locating the relative position of a pulse even when the amplitude has fallen somewhat below the noise level. Using computer software, the received pulse is cross-correlated with a standard pulse of the same frequency consisting of 3-6 complete sine cycles. This cross-correlation substantially removes random noise and the distortions of the received waveform, which may occur close to the critical point. The computer then tracks a zero crossing of the **correlated** signal as the pressure is slowly changed. A zero crossing that occurs in a region where the envelope of the correlation is at a maximum is used. This zero crossing provides a very precise measurement of the "relative" delay (Δt_{rel}) of the received pulse (Fig. 2b).

The ratio of the transmitted pulse amplitude to the received pulse amplitude is determined by the attenuation in passing through the fluid and by the coupling losses at the transducers. These coupling losses depend upon the acoustic impedance, ρw . Both the density ρ and the velocity w vary as the pressure of the fluid is changed. w , however, has already been measured and ρ may be determined from the filled volume and the volume displaced by the piston. These coupling changes may thus be determined and a relative measure of the fluid attenuation calculated.

The acoustic cell is provided with two optical windows, on opposite faces so that phase separation between the ultrasonic transducers may be inspected. To enhance the homogeneity, the fluid mixture is intermittently stirred, under computer control, by the use of a magnetically coupled "flea" located in the bottom of the acoustic cell.

5. RESULTS & CONCLUSIONS

The apparatus has been tested using pure carbon dioxide. The data for the

preliminary measurements is shown in Fig. 3. The preliminary critical point values of 1071 ± 1 PSI and 31.095 ± 0.010 °C measured at 0.97 MHz are close to the accepted data [15]. The velocity values away from the critical point are in good agreement with the data obtained from the NIST Standard Reference Database 12. However, as the critical point is approached the measured velocity can be seen to fall more rapidly than the simulated data, a phenomenon that has been previously noted [9, 15]. At the critical point the velocity has fallen to less than 47% of its atmospheric pressure value. This is one of the deepest minima recorded for carbon dioxide and indicates excellent fluid homogeneity. A fuller account of our search strategies for the critical points will be published in the near future.

This experimentation also indicated a further set of phenomena which influence the measurement of velocity and attenuation very close to a critical point. Since the attenuation rises rapidly as a critical point is approached, it is usual for the transmitting transducer to be driven at high amplitude in this region so that the received signal may still be detected with adequate signal to noise. However the high driven amplitude, when combined with the extremely non-linear acoustic behaviour of the fluid very close to a critical point, ensures that a wealth of non-linear behaviours are encountered there. These include severe distortion of each cycle of the received waveform, and sub-harmonic generation. The latter is the spontaneous generation of frequencies other than that transmitted. A non-linear medium driven at a frequency f by an acoustic wave of sufficient amplitude may generate associated waves at f/n and $f+f/n$ where n is a small integer. Since the attenuation increases rapidly with frequency the sub-harmonic is preferentially received. The effects of these non-linearities are distortions of each cycle of the received waveform and distortion of the received envelope, both increasing in severity as the critical point is approached. These effects make identification of both the exact position of

the received pulse and measurement of its amplitude difficult close to the critical point. In addition there will be fundamental errors in measurements of the attenuation since energy has been extracted from the transmitted wave and corresponding higher order dispersion may slightly affect the velocity.

Whether any of these non-linear affects are *directly* observed depends upon the bandwidth of the receiving transducer and its associated circuitry. Our own transducers are very broad band and both harmonic distortion and the generation of the $f/2$ sub-harmonic may be seen close to a critical point. These non-linear phenomena can be reduced by lowering the amplitude of the voltage driving the transmitting transducer, but this makes it difficult to record data close to the critical point. In finding a compromise there is great advantage in having a transducer bandwidth sufficient to observe the non-linear effects directly.

LIST OF SYMBOLS

P_c = Critical pressure, T_c = Critical temperature, w = Sound velocity, P = Pressure, ρ = density, S = Entropy, V = Specific volume, γ = Ratio of the specific heats at constant temperature to constant volume, T = Absolute temperature, C_v = Specific heat at constant volume, w_{Crit} = Critical point sound velocity, Δt_{abs} = Absolute time of flight, P_x = Amplitude of maxima, N_x = Amplitude of minima, Δt_{rel} = Relative time of flight, and f = frequency.

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FIGURE CAPTIONS

Fig. 1. Schematic diagram of the acoustic apparatus. The bold lines indicate the acoustic circuit, while the thinner lines indicate the environmental control system.

The components are labelled as follows:- PC = LabVIEW controlled computer, TC= Electrical temperature controller, DMM & PRT = Platinum resistance thermometer and digital multimeter, ISCO = ISCO Model 260D syringe pump, TE = Thermal enclosure, P = Fluid driven piston, PT = Pressure transducer, AMP1 = Transmitter power amplifier, AMP2 = Receiver x1000 gain amplifier, CELL = Acoustic cell, MAG = Magnetic stirrer, FG = HP33120A function generator, OSC = TDS220 oscilloscope.

Fig.2. Schematic diagram showing a) the transmitted and b) received pulses (shown on different vertical scales) and c) the method of determining the start of the received pulse from the ratio of the maxima. All three traces are actual signals recorded for CO₂. Where:- T = Transmitted burst, R = Received waveform, t_0 = Start of transmitted pulse, Δt_{abs} = Absolute time of flight, Δt_{rel} = Relative time of flight, N_x = xth minima, P_x = xth maxima.

Fig. 3. a) The sound velocity, measured at 31.095 °C, as a function of pressure (triangles) compared with data from the NIST 12 database (circles).

b) Expanded view close to the critical point.

FIGURE 1.

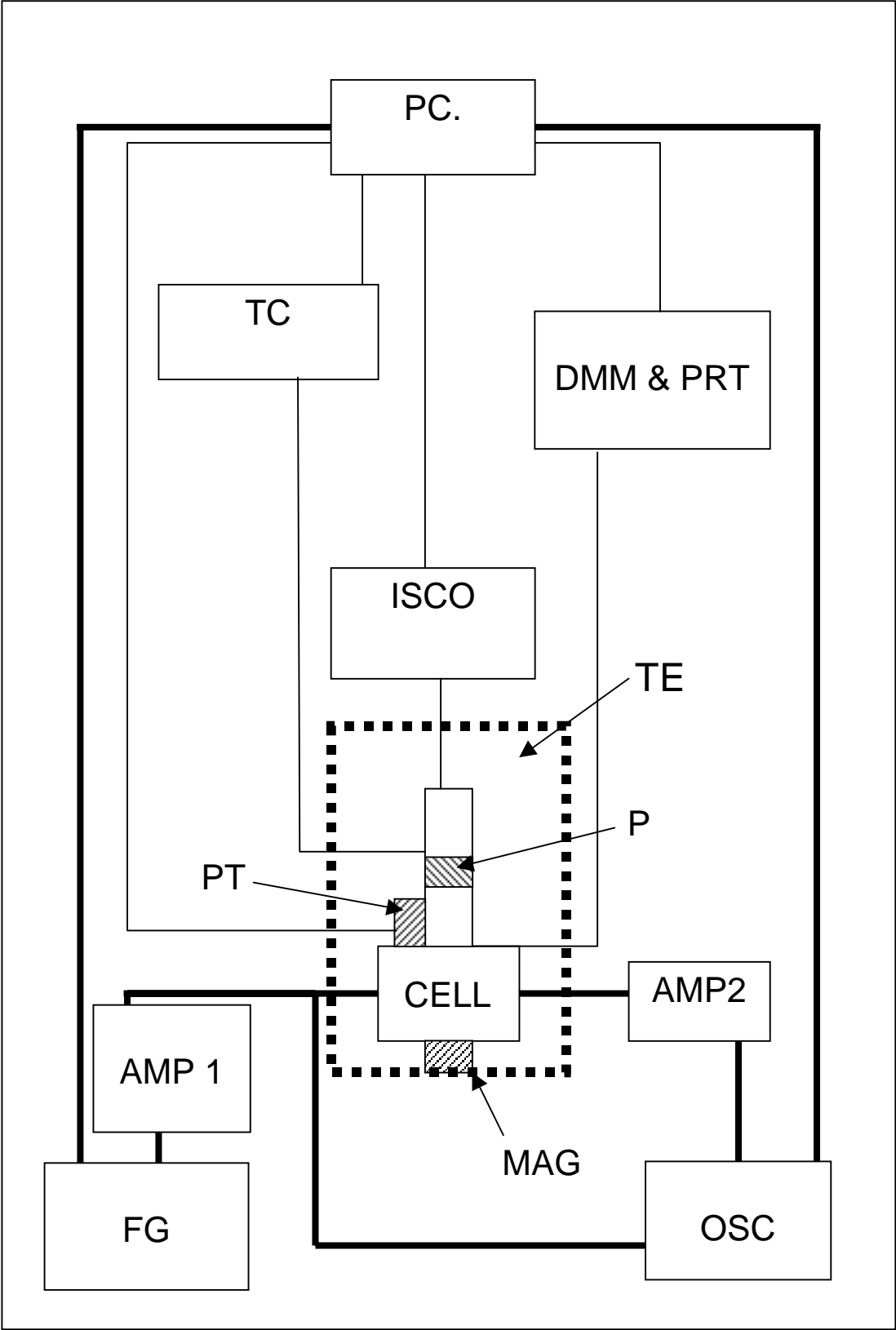


FIGURE 2.

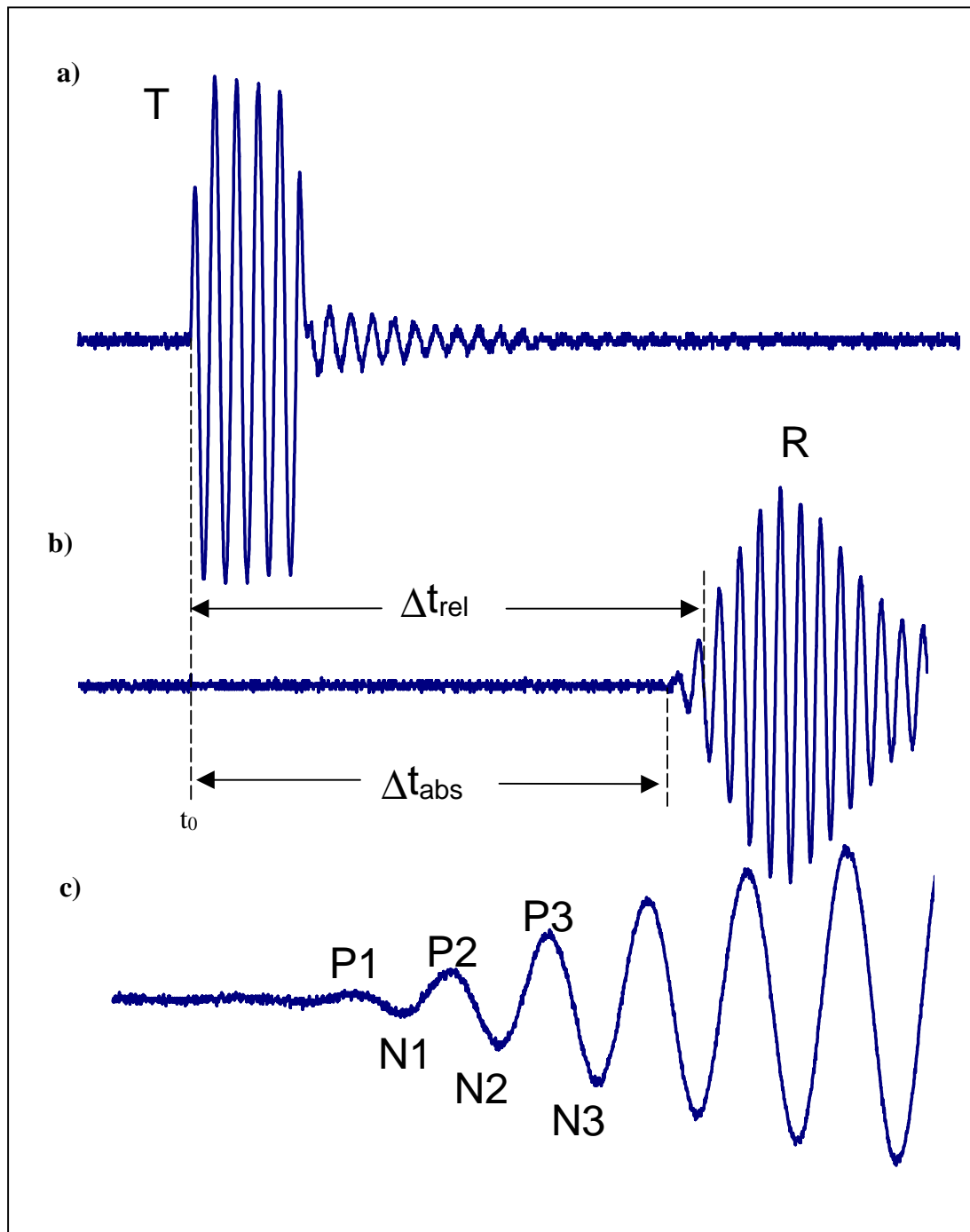


FIGURE 3

